



May 24, 2013

By electronic mail to: [Robert.Kuehn@shell.com](mailto:Robert.Kuehn@shell.com)

Re: Minutes  
Tetra Tech Teleconference with EPA Region 6  
May 23, 2013

Mud and Produced Water Characterization Study to Meet Requirements of the NPDES  
Permit for the Western and Central Gulf of Mexico Outer Continental Shelf (GMG  
290000)

Dear Mr. Kuehn:

The attached minutes reflect the general discussion and decisions made during the teleconference but are not a verbatim record of the meeting. Please let me know if you have any comments or questions about these minutes, or if you prefer another format (office: 504-834-6276; cell: 504 273-9186; [june.mire@tetrattech.com](mailto:june.mire@tetrattech.com)).

A handwritten signature in black ink, appearing to read 'June B. Mire'.

June B. Mire, Ph.D.  
Project Manager

Attachment

## Participants:

### EPA Region 6

Isaac Chen  
Taimur Shaikh

### Tetra Tech

June Mire  
Jessica Vickers  
Alberto Tohmé  
Jim Collins  
Randy Bassett

## Agreements and Decisions

### Holding Time for Unfiltered Produced Water Sample

Samples of produced water will be collected on the rig platform by operator personnel according to approved EPA procedures and sent to the lab for filtration. EPA agrees that an elapsed time of 48 hours from time of produced water collection to stabilization of the filtered sample in the lab would not require any qualification of the results for dissolved hexavalent chromium. Any produced water sample that was not filtered and stabilized within 48 hours of collection would be discarded. As a back-up plan for obtaining analytical results for samples that exceed the 48-hr holding time (due to unforeseen delays), Tetra Tech is considering collecting a second sample of produced water in a container preserved with a buffer solution that would extend the holding time to 14 days (for total hexavalent chromium, using EPA Method 218.7). In the unfortunate event that the holding time on the unpreserved sample expires before it can be filtered and stabilized, the preserved sample would be analyzed for total rather than dissolved hexavalent chromium. Both EPA and Tetra Tech are conducting literature reviews to develop a reasonable approach to interpreting any results on total hexavalent chromium with respect to national ambient water quality criteria.

If the OOC wants to explore the option of exceeding the 48-hour holding time for dissolved hexavalent chromium, EPA would like to see justification in the form of a literature review or a separate study using split samples to demonstrate the effect of various holding times on dissolved hexavalent chromium concentrations.

### Holding Time for Water Based Mud (WBM)

Samples of WBM will be collected and sent to the lab for centrifugation and analysis of the extracted aqueous portion. EPA agrees that an elapsed time of 48 hours from time of WBM collection to stabilization of the aqueous sample in the lab would not require any qualification of the results for hexavalent chromium.



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### **Piggybacking on the Suspended Particulate Phase of the WBM Sample Used for Monthly Toxicity Testing**

The purpose of the characterization study is to provide data that EPA will use to prepare a Reasonable Potential analysis, which is based on water quality criteria for dissolved metals. The samples used for toxicity testing are not filtered and are not representative of the WBM or produced water samples to be used for the Reasonable Potential analysis. Therefore, EPA stated that the samples used for toxicity testing are not suitable for the characterization study.

### **Action Items**

Tetra Tech and EPA will each conduct a brief literature review on the effect of holding times of dissolved hexavalent chromium concentrations in produced water (or sea water). We will also search for information on the relationship between dissolved and total hexavalent chromium in produced water (or sea water).

At Tetra Tech's request, EPA agreed to review the draft sampling and analysis plan prior to the OOC initiating any sampling. However, EPA emphasized that the OOC is not required to wait for EPA approval before initiating sampling.

## **Summary of February 25 Teleconference on the Mud and Produced Water Characterization Study Being Carried out for NPDES Permit GMG290000**

A teleconference was held on February 25, 2014 to discuss an alteration in the study plan for the Water Based Mud and Produced Water Characterization Study (the "Study") being carried out by a group of Gulf of Mexico operators to meet their requirements for water based drilling fluid and produced water characterization under NPDES Permit GMG290000. The participants in the call were Taimur Sheikh and Isaac Chen (EPA Region 6), Joseph Smith (ExxonMobil Upstream Research Company, representing the Study participants, June Mire and Len Nelms (both of Tetra Tech Inc., contractor for the Study).

### **Background**

NPDES Permit GMG290000 requires analysis of the dissolved concentrations of certain components in water based drilling mud. It has proved to be difficult to get an adequate volume of water from water based drilling mud for analysis of soluble components. This difficulty arises because the muds are formulated to be stable suspensions and to resist filtration so that they can have the desired operational properties.

The study participants and Tetra Tech asked to have a discussion of possible solutions to this problem with EPA Region 6 so that EPA would be informed of the need to change the original study plan.

### **Discussion Notes**

The study participants and Tetra Tech have considered analyzing the total concentrations of the target analytes in drilling mud (as opposed to the dissolved concentrations) as well as diluting the mud with deionized water or artificial seawater to facilitate obtaining a sample of the dissolved phase of the drilling mud. EPA Region 6 expressed a preference for avoiding dilution. The group acknowledged uncertainties associated with developing equilibrium coefficients for such a large set of variable drilling mud formulations.

It was agreed that the total concentrations of target analytes in drilling mud would be determined using SW 6020. In cases where sufficient water can be extracted from the drilling mud without dilution, the concentrations of dissolved components will be determined to help understand the correlation between dissolved and total concentrations in the drilling mud.

Determination of dissolved concentrations requires separate analyses for metals, hexavalent chromium, and cyanide. It was agreed that in situations where water could be extracted from drilling mud, the water would be used to determine concentrations of hexavalent chromium first, then metals. Cyanide will not be analyzed. The group discussed the wisdom of changing analytical methods to use instruments that require less water volume, such as gas furnace atomic absorption spectroscopy, but determined that such a change was not warranted.

The occurrence of cyanide in drilling fluid is considered highly unlikely. EPA requested that the operators provide them with information on the use of materials containing cyanide in water based drilling mud.

It was agreed that the results of samples already analyzed using dilution with deionized water would be reported to EPA as a separate data set. Any available residual samples of previously analyzed drilling muds will be subjected to a determination of total concentrations of metals if sufficient sample volume is available.

#### **Follow Up After the Teleconference**

Follow up conversations with drilling fluid suppliers and a brief search of the literature supported the view that the occurrence of cyanide in drilling fluids was highly unlikely. Discussions with drilling fluid suppliers indicated that materials with cyanide are not deliberately added to drilling fluids. A brief search of the literature failed to turn up any studies that showed the presence of cyanide in drilling fluids.



May 21, 2014

By electronic mail to: [chen.isaac@epa.gov](mailto:chen.isaac@epa.gov); [shaikh.taimur@epa.gov](mailto:shaikh.taimur@epa.gov)

**Re: Comparison of Produced Water Samples Preserved in the Field and in the Lab:  
Joint Industry Project (JIP) Mud and Produced Water Characterization Study to Meet  
Requirements of the NPDES Permit for the Western and Central Gulf of Mexico Outer  
Continental Shelf (GMG 290000)**

Dear Mr. Chen and Dr. Taimur:

On behalf of the Offshore Operators Committee, we are submitting this evaluation of the results of dissolved constituent analysis of produced water samples filtered and preserved on site compared with results for samples filtered and preserved in the laboratory. This letter report details the findings of this comparison evaluation, as well as our recommendation to discontinue the on-site filtration and preservation of the samples.

## **BACKGROUND**

As discussed in the Sampling and Analysis Plan and Quality Assurance Project Plan (SAP/QAPP), Revision 01, the produced water samples have been filtered on-site using a peristaltic pump and collected in pre-preserved containers. Samples have been preserved in the field to address concerns that the concentration of hexavalent chromium may differ between samples preserved in the field and samples preserved in the laboratory. The analytical method requires that filtration occur prior to adding preservative. Therefore, samples were filtered in the field. The filtering has been performed on-site in an effort to extend the holding time for hexavalent chromium to accommodate logistical challenges in transporting samples from offshore platforms to the laboratory.

The numerous challenges of field-filtering water samples across the offshore operations led the OOC to investigate the differences in analytical results in field-preserved and lab-preserved produced water samples. No correlational data for field-preserved versus lab-preserved dissolved metals, hexavalent chromium, or cyanide could be located in the literature. Therefore, we conducted a split-sample study to compare these two types of sample preparation for produced water. At the randomly selected 21 discharges included in the study, two identical produced water samples were collected. One sample of each pair was filtered and preserved as described in the SAP/QAPP. The other sample was collected into an unpreserved container without being filtered. The unfiltered/unpreserved samples were filtered and preserved when they were received at the laboratory. All samples were then analyzed for the dissolved phase of the analytes of concern for this study – arsenic, cadmium, copper, cyanide, hexavalent chromium, lead, mercury, nickel, selenium, silver, and zinc.

## **OVERALL ASSESSMENT OF COMPARISON DATA**

Concentrations of dissolved metals in field-preserved and lab-preserved sample pairs were compared. For all detected analytes, the relative percent difference (RPD) in concentration of each pair was calculated. The criteria used for comparison was a RPD of greater than 20 percent for results greater than highest reporting limit. These criteria are discussed in the EPA Contract Laboratory Program (CLP) National Functional Guidelines (NFG) for Inorganic Superfund Data Review (January 2010)<sup>1</sup>. Note that the

<sup>1</sup> <http://www.epa.gov/superfund/programs/clp/guidance.htm>

criteria in the EPA CLP NFG (2010) were developed for evaluating duplicate/replicate values from a single sample location

We analyzed 21 pairs of produced water samples for the following dissolved constituents: arsenic, cadmium, copper, lead, nickel, selenium, silver, zinc, hexavalent chromium, mercury, and cyanide. The most frequently detected metal was zinc, which was detected in 11 of the 21 samples. Lead was detected in one sample. Arsenic was detected in one sample and estimated in another sample. Cadmium, copper, nickel, selenium, silver, hexavalent chromium, mercury, and cyanide were not detected in any sample (Enclosure 1).

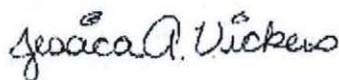
In general, except for a two pairs, the two types of sample preparation were within acceptance criteria. The overall concentrations of dissolved metals in this preliminary dataset indicate that none of the produced water samples would exceed the recommended Ambient Water Quality Criteria after post-discharge mixing is accounted for. These observations suggest that filtering and preserving the samples in the field is not warranted. Because of the logistical difficulties posed by filtering and preserving samples in the field (including shipment and maintenance of peristaltic pumps), Tetra Tech requests EPA's concurrence in our recommendation to discontinue on-site filtration and preservation of produced water samples. Samples would be filtered and preserved when received by the lab.

Please contact June Mire at (504) 834-6276 or Jessica Vickers at (662) 681-5727 if you have any questions or comments on this recommendation. We look forward to discussing these results with you.

Sincerely,



June B. Mire, Ph.D.  
Project Manager  
[june.mire@tetrattech.com](mailto:june.mire@tetrattech.com)



Jessica A. Vickers  
Laboratory/Analytical/Data Quality Leader  
[jessica.vickers@tetrattech.com](mailto:jessica.vickers@tetrattech.com)

Enclosure

cc: OOC Core Team

**ENCLOSURE 1**

**COMPARISON OF SPLIT SAMPLE RESULTS  
PRODUCED WATER SAMPLING  
DETECTED RESULTS ONLY  
2013 - 2014**

(One Page)



Analyte <sup>1</sup>	Sample Preparation		Relative Percent Difference
	Field Preserved Result (mg/L)	Lab Preserved Result (mg/L)	
Dissolved arsenic	<b>0.0614</b>	<b>0.00753</b>	<b>156</b>
	ND	ND	NC
	ND	ND	NC
	ND	ND	NC
Dissolved lead	1.86	1.67	10.8
Dissolved selenium	ND	ND	NC
	ND	ND	NC
	ND	ND	NC
	ND	ND	NC
	0.00570	ND	NC
	ND	ND	NC
Dissolved zinc	<b>0.00857</b>	<b>0.0152</b>	<b>55.8</b>
	0.0163	0.0147	10.3
	0.00982	0.0106	7.6
	12.7	11.9	6.5
	0.336	0.355	5.5
	0.116	0.122	5.0
	0.0495	0.0510	3.0
	0.280	0.273	2.5
	14.6	14.8	1.4
	0.529	0.529	0.0
	ND	ND	NC
	ND	ND	NC
	0.266	ND	NC
	ND	ND	NC
	ND	ND	NC
	ND	ND	NC
	ND	ND	NC

<sup>1</sup> 21 pairs of produced water samples were analyzed for dissolved arsenic, cadmium, copper, lead, nickel, selenium, silver, zinc, hexavalent chromium, mercury, and cyanide. Cadmium, copper, nickel, silver, hexavalent chromium, mercury, and cyanide were not detected in any sample.

**BOLD** The relative percent difference exceeds the precision criterion.

mg/L Milligrams per liter

NC The relative percent difference was not calculated because at least one of the results was non-detect.

ND The analyte was not detected at or above the reporting limit.

**From:** [Mire, June](#)  
**To:** [shaikh.taimur@epa.gov](mailto:shaikh.taimur@epa.gov); [chen.isaac@epa.gov](mailto:chen.isaac@epa.gov); [Vickers, Jessica](#); [ileana.rhodes@shell.com](mailto:ileana.rhodes@shell.com); [robert.kuehn@shell.com](mailto:robert.kuehn@shell.com); [gkorenaga@chevron.com](mailto:gkorenaga@chevron.com); [joe.p.smith@exxonmobil.com](mailto:joe.p.smith@exxonmobil.com)  
**Subject:** OOC Produced Water Protocol Change  
**Date:** Monday, June 09, 2014 4:35:36 PM

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Isaac and Taimur,

Thank you for making the time to talk with us today. This email documents the discussion and conclusions of our call on the protocol for collecting produced water samples as part of the Joint Industry Program.

**Participants:** Isaac Chen (EPA), Taimur Shaikh (EPA), Rob Kuehn (Shell), Gail Korenaga (Chevron), Jessica Vickers (Tetra Tech), June Mire (Tetra Tech)

**Background:**

1. No consistent trend in metals concentrations was observed between field-filtered and lab-filtered produced water samples.
2. Most constituents were not detected in either field-filtered or lab-filtered samples.
3. Laboratory filtration offers benefits of better pumps, more consistent personnel, more quality control, and potentially more representative equilibria.

**Decision:**

1. Field filtering of produced water samples can be discontinued immediately.
2. Samples should be collected with near-zero head space.

**Other topics:**

- When a lease area has too few produced water discharges to meet the desired distribution of 10 separate blocks, we have been collecting repeated produced water samples from the same platform(s) on different days. All agreed that this is an acceptable way to obtain the required 10 samples per lease area.
- We anticipate collecting our last samples in April, 2015 and submitting the report to EPA in October, 2015.

**June B. Mire, Ph.D.** | Senior Ecologist and Project Manager  
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